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Linking sediment geochemistry with catchment processes, internal phosphorus loading and lake water quality

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ABSTRACT

Research in the field of sediment geochemistry suggests potential linkages between catchment processes (land use), internal phosphorus (P) loading and lake water quality, but evidence is still poorly quantified due to a limited amount of data. Here we address the issues based on a comprehensive data set from 27 lakes in southern Finland. Specifically, we aimed at: 1) elucidating factors behind spatial variations in sediment geochemistry; 2) assessing the impact of diagenetic transformation on sediment P regeneration across lakes based on the changes in the vertical distribution of sediment components; 3) exploring the role of the sediment P forms in internal P loading (IL), and 4) determining the impact of IL on lake water quality. The relationship between sediment P concentration and field area percentage (FA%) was statistically significant in (mainly eutrophic) lakes with catchments that included more than 10 % of fields. We found that sediment iron-bound P (Fe-P) increased with increasing FA%, which agrees with the high expected losses from the cultivated areas. Additionally, populated areas increased the pool of sediment Fe-P. Internal P loading was significantly positively related to both sediment Fe-P and sediment organic P (Org-P). However, Org-P was not significant (as the third predictor) in models that had a trophic state variable as the first predictor and Fe-P as the second predictor. Further, the vertical profiles of sediment components indicated a role of diagenetic transformations in the long-term sediment P release, especially in lakes with deeper maximum depth and longer water residence time. Finally, IL was significantly positively correlated to water quality variables including phytoplankton biomass, its proportion of cyanobacteria, chlorophyll *a* concentration and trophic state index. Our findings suggest that reduction of P losses from the field and populated areas will decrease internal P loads and increase water quality through a reduced pool of Fe-P.

1. Introduction

Bottom sediment is an important compartment of lake ecosystems. It serves as a depository for many organic and inorganic components that are transported from the catchment or produced within the waterbody (Waters et al., 2023). These components can be recycled to the overlying water column, influencing water quality. Several studies have found linkages between the geochemical composition of the upper sediment layers and water quality variables (Albright et al., 2022; Waters et al., 2023). One of the important processes associated with lake eutrophication is internal phosphorus (P) loading (Steinman and Spears, 2020). It has often delayed the response of lake water quality to reduced external nutrient supply (Jeppesen et al., 2005; McCrackin et al., 2016; Rippey et al., 2022) highlighting the need for measures that also reduce sediment P release. The effectiveness of these measures is improved with thorough understanding of the factors involved in internal P loading.

Classically, sediment P release has been associated with the reduction of ferric to ferrous iron and the subsequent dissolution of the

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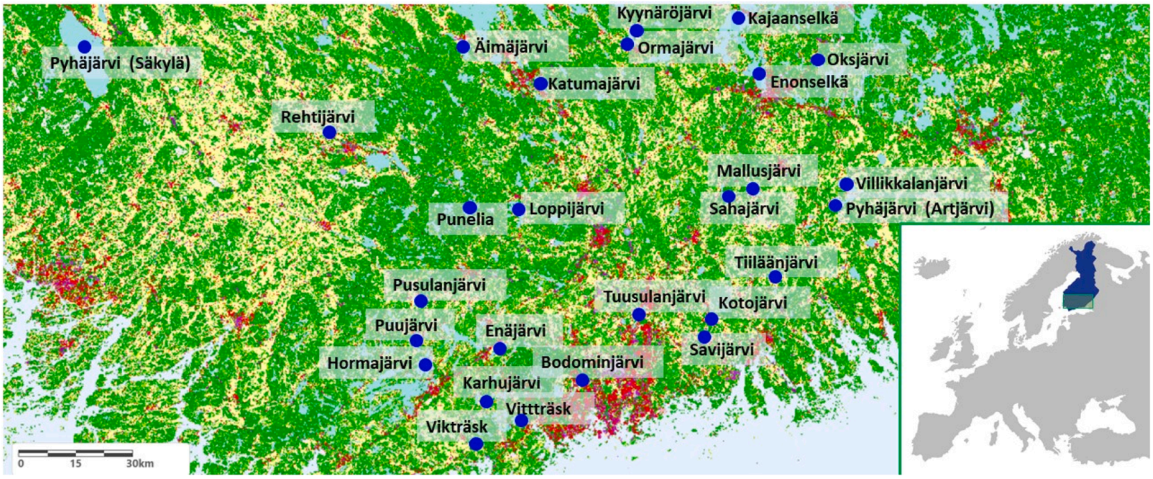

Fig. 1. Location and land use of the study area. Study lakes (blue filled circles), urban areas (red), forest areas (green), field areas (yellow) are shown. Map ranges N 60°40′ (N 60°17′) and E 27°15′ (N 27°21′). For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

adsorbed phosphate. Furthermore, Nürnberg (1988; 2020) has demonstrated a relationship between sediment P release rate and the concentration of iron-bound P (Fe-P), indicating that reductive dissolution is a ubiquitous mechanism, irrespectively of the trophic state of a lake. Correspondingly, the higher P release rate in lakes with higher trophic state is related to a larger pool of redox-sensitive P. Further, the process is influenced by the extent of anoxia, which can be described by the anoxic area factor (Nürnberg, 2009). Anoxia advances with increasing water temperature, stability, and mineralization of settled organic matter (Gächter and Wehrli, 1998). P may also be released directly from decomposing organic matter (Rydin, 2000; Wang et al., 2022), a process that is particularly recognised in highly eutrophic lakes (e.g., Liu et al., 2023; Ma et al., 2023). Fe-P and Org-P form a pool of potentially mobile P, and the diagenetic processes (determined from the P changes with sediment depth) regulate sediment P release from the pool in the long-term (Carignan and Flett, 1981; Trolle et al., 2010; Carey and Rydin, 2011).

Sediment geochemistry that affects water quality likely reflects catchment activities. In general, the correlations between land use characteristics and trophic state are well-established, whereby lakes with watersheds dominated by cropland are characterized by higher trophy (Carter and Dzialowski, 2012). Laakso et al. (2023) reported contrasting geochemical profiles for three lakes of southwestern Finland with different trophic state (oligotrophic, mesotrophic and eutrophic). The authors reported net diffusive flux (P release) in mesotrophic and eutrophic lakes that received nutrient loading from agricultural land. Moreover, Carter and Dzialowski (2012) demonstrated that sediment P release rates were positively related with the cropland % in the watershed. The authors emphasized the benefit of models based on readily available land use data, not requiring field sampling or laboratory

Table 1

The morphometric and land use variables for 27 lakes of southern Finland. The trophic is state is classified as "mesotrophic", "eutrophic" and "hypertrophic" if the lake water average TP concentration is 10–30 μg/l, 30–100 μg/l, and >100 μg/l, respectively.

Lake	Lake area km^2	Catchment area km^2	Mean depth m	Maximum depth m	Water residence time 1/y	Trophic state	Field area %	Forest area %	Populated area %
Bodominjärvi	4.1	32	4.3	12.7	1.94	eutrophic	19	42.1	4.6
Enäjärvi	4.9	34	3.2	9.1	1.62	eutrophic	22	36.4	11.4
Enonselkä	26	84	6.8	33	7.42	eutrophic	24.4		
Hormajärvi	5.1	16	7.3	21	8.20	mesotrophic	7.3	46.8	2
Kajaanselkä	44	138	6.8	42	7.64	mesotrophic	17.9		
Karhujärvi	1.9	142	2.2	4.9	0.10	eutrophic	15	52.5	
Katumajärvi	3.8	51	7.1	18.9	1.86	mesotrophic	7.8	53.6	5
Kotojärvi	1.48	22.06	3.34	8	0.79	hypertrophic	17.6	57.1	3.6
Kyynäröjärvi	0.25	25	1.3	3	0.05	eutrophic	26	60.9	1.2
Loppijärvi	11.8	82	1.8	6.7	0.91	eutrophic	14	53.2	1.8
Mallusjärvi	5.4	88	4.1	8.83	0.89	eutrophic	25.7	51.7	1.4
Oksjärvi	2.48	27.7	5.69	14.06	1.79	mesotrophic	9.9	61.1	1.8
Ormajärvi	6.6	86	9.6	29.4	2.60	mesotrophic	25.3	46.6	3.8
Punelia	6.8	102	3.8	14	0.89	mesotrophic	1.7	66.1	0.3
Pusulanjärvi	2.1	226	4.9	10.6	0.16	eutrophic	15	59.9	1.5
Puujärvi	6.4	27	8.3	21.7	6.93	mesotrophic	15	47.4	1.7
Pyhäjärvi (Artjärvi)	12.9	459	21	68	2.08	eutrophic	31	48.4	1.7
Pyhäjärvi (Säkylä)	155	461	5.5	26.2	6.52	mesotrophic	21	44.3	1.4
Rehtijärvi	0.4	3	9.2	30	4.32	eutrophic	55		
Sahajärvi	1.92	26	4.3	11	1.12	eutrophic	18.7	54.5	1.3
Savijärvi	0.4	3	1.6	2.6	0.75	eutrophic	14.8		
Tiiläänjärvi	2.1	38	4.4	10.3	0.86	eutrophic	22	54.3	1.1
Tuusulanjärvi	5.9	92	3.2	10	0.72	eutrophic	28	33.2	13.8
Vikträsk	1.87	487	4.49	15	0.06	eutrophic	22	48.9	4.7
Villikkalanjärvi	7.1	413	3.2	10	0.19	hypertrophic	31	50.7	1.7
Vitträsk	4.9	10.2	9.21	21.65	15.59	mesotrophic	1	36.2	
Äimäjärvi	8.5	93	2.9	9	0.93	eutrophic	13.2	56.3	2.9

experiments. Land use and sediment P release rate are hypothetically linked through sediment geochemistry, which may explain the impact of specific P forms on water quality. Applications of models integrating both, catchment characteristics (e.g., proportion of field area) and sediment characteristics, for water quality management may be particularly important when watershed area is large compared to lake area.

In the current study, we used our sediment, water quality and land use data for 27 lakes of southern Finland to: 1) elucidate factors behind the spatial variation in sediment geochemistry; 2) to assess the impact of diagenetic transformation in sediment P regeneration across lakes based on the changes in the vertical distribution of sediment chemicals; and 3) to explore the role of different sediment P forms in internal P loading. In particular, we analyzed relationships between specific P forms with internal P load and with the portion of lake water TP concentration that is associated with internal P loads (predicted by a mass balance model). We hypothesized that the variation in sediment P among lakes correlates positively with the percentage of the field area in the catchment.

2. Materials and methods

2.1. Study lakes and area

The study area includes 27 lakes with surface areas ranging from 0.25 to 155 km^2 located in southern Finland (Fig. 1) with mean depth from 1.3 to 21.0 m and maximum depth from 3 to 68 m (Table 1). Most of the lakes have deep stratifying regions, which undergo periodic anoxia, generally in winter and during thermal stratification in summer. The monitoring data (Hertta data set, Finnish Environment Institute; averaged over the period 1985–2014) indicates the trophic status ranging from mesotrophic to hypereutrophic (as defined in Nürnberg (1996); Table 1). The long-term (1985–2014) growing season (May–October) mean for total phosphorus concentration (TP) ranged from 12 to 200 μg/l (average 52 μg/l), chlorophyll *a* concentration (Chl *a*) from 3 to 50 μg/l (average 18 μg/l), phytoplankton biomass (BM) from 0.5 to 31 mg/l (average 5 mg/l), proportion of cyanobacteria (CY%) in total phytoplankton biomass from 1 % to 60 % (average 20 %), and trophic state index (TSI) from −1.3 to 2.5 (average 1.1). The water color in study lakes varied from 10 to 230 mg/l Pt, being higher in lakes with higher trophy and smaller size.

The percentage of the field area ranged from 1 % to 55 % being generally lower in the catchments of the mesotrophic lakes and higher in the catchments of eutrophic lakes. Human impact is reflected by the percentage of populated and paved areas, being lowest in the catchment of Lake Punelia (Appendix Table 1). The forest% of the catchment ranged from 36 % to 66 % (Table 1). The mean external P load values representative of the study period (collated from a number of reports by Tammeorg et al. (2017)) for the study lakes were highly variable and ranged from 25 to 2380 mg/m^2/y.

In southern Finland, a key source of detrital material to modern lake sediments is erosion of clay-rich soils in catchment areas. These soils are derived mainly from glacio-lacustrine and glacio-marine sediments deposited in quiescent subaqueous conditions following the retreat of the Fennoscandian ice sheet (Saresma et al., 2021), which have been exposed due to isostatic rebound (Taipale and Saarnisto, 1991). The deposits are typically a few meters to tens of meters thick, with a composition dominated by clay minerals such as illite and chlorite (Gardemeister, 1975). Soil formation processes have led to the development of cambisols with accumulation of iron oxides in the uppermost layers (Schwertmann, 1993) leading to a strong binding capacity for P (Saarela, 2002). Additional sources of detrital material to lake sediments occur through erosion of glacial till and thinner coarse-grained podzol soils in areas of higher elevation that did not accumulate clay deposits during the retreat of the ice sheet.

2.2. Sampling and chemical analyses

Sediment cores were collected with a HTH gravity corer from the deepest site of each lake targeting the accumulation areas (Håkanson and Jansson, 1983). Sediments were sampled in March 2013 and 2014, when the lakes were ice-covered to avoid core disturbances (e.g., due to wind activity, bioturbation, temperature). The top 20 cm of each core was sectioned into 2-cm slices, yielding 10 samples per core. Dating of cores from 20 lakes (by ^{210}Pb and ^{137}Cs) indicated that the sediments accumulated over two to three decades (Tammeorg et al., 2017; 2018). All sediment samples were freeze-dried and ground. The TP concentrations from the sediment subsamples were determined using the methods by Koroleff (1979); Lachat autoanalyzer, QuickChem Series 8000; Lachat instruments, Loveland, USA) after wet digestion with sulphuric acid and hydrogen peroxide (Milestone Ethos 1600 microwave oven; Milestone, Sorisole, Italy).

Sediment P fractional composition was determined as described by Ruban et al. (1999), after a modified protocol of Williams et al. (1980). This method uses NaOH to solubilize Fe, and HCl to dissolve Ca. The extraction procedure results in the following fractions: Fe-bound P (Fe-P), Ca-bound P (Ca-P), inorganic P (IP), organic P (Org-P, partly available), and total P (TP). To quantify the organic matter of the sediment, loss on ignition (LOI) was determined by drying sediment samples at 105 °C for about four hours and then heating them at 550 °C for two hours (Heiri et al., 2001). For further sediment analysis, the ash was transferred into an Erlenmeyer flask with 50 ml 0.2 M HCl, heated until less than 25 ml was left, transferred quantitatively into a 50-ml measurement flask, adjusted to volume with deionized water and finally filtered through an ashless filter paper (Whatman, Grade 589/3, blue ribbon, pore size <2 μm, GE Healthcare, UK). The concentrations of a number of elements including P, K, S, Ca, Mg, Na Al, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Sr, Zn were determined by ICP-OES, and final concentrations were expressed per sediment dry weight. These elements were analyzed for the potential to indicate human impact, including toxicity. The C and N content was determined by Dumas combustion for the uppermost (0–2 cm) sediment layers.

2.3. Calculations and statistical analyses

To determine the causes of variations in sediment P and internal P load, relationships between the sediment P forms and lake morphometric characteristics, anoxia (as anoxic factor), land use data, and external P load were analyzed (Pearson′s correlations). Also, the relationships between several sediment P forms and other sediment components were studied. Data were log-transformed before the analysis, when necessary, to ensure the normal distribution of residuals (by Shapiro–Wilk test). The percentage of field area to catchment area (FA %), and field area relative to lake surface area (FA/LA) were both identified as important predictors of external P loading in the lakes of southern Finland (Horppila et al., 2019), and thus were of particular interest. Land use data were obtained using the VALUE tool provided by the Finnish Environment Institute (http://paikkatieto.ymparisto.fi/value). The tool derives land use variables and lake percentages from Coordination of Information on the Environment (CORINE) 2012 land cover data.

Vertical changes (0–20 cm) in the distribution of sediment P and other components (decreases, increases or no change) were studied with the linear regression model.

Internal P loading (IL) was calculated as hypolimnetic accumulation for deeper stratifying lakes (Tammeorg et al., 2017), with the following exceptions. In Enäjärvi and Rehtijärvi, the method resulted in estimates inconsistent with their trophic state (order of magnitude lower than in other eutrophic lakes in Enäjärvi and an order of magnitude higher than in other eutrophic lakes in Rehtijärvi). Thus, in these two eutrophic lakes, the internal P load was estimated based on the product of anoxic factor (AF) and P release rate (RR) using the average RR of 10.8

Table 2

Significant correlations (Pearson's) between the sediment variables ($n = 27$), internal P load (IL), external P load (EL) and lake morphometric and catchment variables. Lake morphometric variables included lake mean depth (D) and maximum depth (Dmax), lake area size (LA), catchment area (CA), water residence time (tau). Catchment variables included proportion of fields (FA%), populated areas (POP%), paved areas (PAV%), forests (FOR%), and wetlands (WET%) in the catchment, but also their areas relative to the lake surface areas. Anoxic factor (AF_{pred}) is the modelled measure of anoxia. Statistically more robust relationships are likely, if there is no lake area on both sides of the relationships. For example, the relationship between FA% and EL expressed in kg/yr verifies the relationship between FA% and EL expressed in mg/m^2/y. Sediment variables include iron-bound P (Fe-P), organic P (Org-P), calcium-bound P (Ca-P), organic matter content expressed as loss-on-ignition (LOI).

	EL (mg/m^2/y)	EL (kg/y)	IL (mg/m^2/y)	Fe–P (mg/g)	Org-P (mg/g)	Ca–P (mg/g)	LOI (%)
FA%	0.661***	0.530**					
FA/LA	0.860***	0.534**					
POP%			0.471*	0.486*			
POP/LA	0.776***		0.489*				
PAV%							
PAV/LA	0.775***	0.521*					
FOR%				−0.425*			
FOR/LA	0.719***						
WET%					0.488*		
WET/LA	0.578**	0.494*					
CA (km^2)		0.816***				0.536**	
LA (km^2)	−0.432*	0.485*	−0.507**			0.585**	
D (m)				0.442*			
D_{max} (m)			−0.393*	0.464*			
Tau (1/y)	−0.690***			0.468*			
EL (mg/m^2/y)		0.533**			−0.400*		−0.407*
EL (kg/y)						0.438*	−0.486*

mg/m^2/d reported for eutrophic lakes (Nürnberg, 2020), similar to the method applied in Tammeorg et al. (2020). Using this method, IL values for the lakes were similar to those of the other lakes. By the same method, IL was calculated for the lakes Vitttäsk, Vikträsk and Oksjärvi, because low sampling frequency in these lakes did not allow us to quantify hypolimnetic P accumulation. Further, the AF*RR method was used for the lakes that are very eutrophic, shallow and mixed (Karhujärvi, Savijärvi, Loppijärvi and Kyynäröjärvi), where sediment surfaces may be anoxic despite aerated/oxic water column.

The anoxic factor represents the temporal and spatial extent of the sediment area in a lake potentially involved in P release and is modelled as AF_{pred} – summer AF (in days per summer) (Nürnberg, 2004):

$$AF_{pred} = -36.2 + 50.1\log(TP_{sum}) + 0.762z / LA^{0.5}, \tag{1}$$

where z – mean depth (m); LA – lake surface area (km^2); TP_{sum} – epilimnetic TP concentration in summer (μg/l). Mean depth divided by the square root of lake surface area is also known as morphometric ratio, reflecting water column stability.

AF_{pred} was calculated for all study lakes because it more adequately describes anoxia at the sediment water interface in lakes with only small parts of stratification where anoxia of sediment surfaces can extend further than in the water column (Tammeorg et al., 2020). Thus, we used modelled AF values for both shallow (polymictic) and stratifying lakes.

The TP concentration in the lake water that can be associated with internal P load (TP-dif) was computed as the difference between observed surface water (epilimnetic) TP concentration (TP_{obs}) and TP concentration predicted from Eq. (2) (TP_{pred}) (Nürnberg, 2020).

$$TP_{pred} = EL / q_s * (1 - R_{pred}) \tag{2}$$

where EL is external TP load (in mg/m^2/y), q_s is annual areal water load (m/y), and R_{pred} is TP retention due to sedimentation, predictable for many lakes using the parameters $R_{pred} = 15/(18 + q_s)$. Eq. (2) does not consider internal P load; thus, it predicts minimum summer epilimnetic TP concentration (TP_{pred}), close to early summer concentration averages. For the study lakes, May–October mean TP (52 μg/l) was not significantly different from annual mean TP values (49 μg/l) for the surface (epilimnetic) water layer. We used summer mean TP values as TP_{obs}, and assumed that the difference between TP_{obs} and TP_{pred} (i.e., difference between late and early summer TP concentration) is attributable to sediment P release. TP-dif for Kotojärvi was much higher than for the rest of the lakes for unknown reasons and was excluded from the following analyses.

The relationships between the sediment P forms (0–10 cm average Fe-P, Org-P, TP) and IL and TP-dif were studied to determine the potential drivers of IL. The relationships of IL and TP-dif with the key water quality variables (Chl *a*, BM, CY%, TPI) were investigated to determine their potential effects on water quality. Means of the whole growing season (May–October) for the long-term period (1984–2014, i.e. approximately the period equivalent to the length of the sediment core profiles) were used.

3. Results

3.1. Variation in the sediment variables of 27 lakes and linkage to the catchment

Sediment Fe-P concentration (0–10 cm average) varied from 0.29 (Lake Punelia) to 2.72 mg/g dry weight (Hormajärvi) (average 0.83 mg/g; Appendix Table 2), contributing from 28 % to 84 % (55 % on average) to sediment TP (Fe-P%) in the study lakes. Being the main contributor to the sediment TP in most of the lakes, sediment Fe-P concentration was highly significantly correlated with TP concentration ($r = 0.901$, $p < 0.001$). Fe-P% was lowest (28 %) in the sediments of Lake Punelia with the lowest human impact in the catchment (Appendix Table 1). The highest Fe-P% was observed in Hormajärvi (84 %), perhaps due to increased sorption of P by Fe promoted by the recent hypolimnetic aeration treatment. Interestingly, sediments of Punelia had also the lowest (16 mg/g) and sediments of Hormajärvi the highest concentrations of Fe (28 mg/g; Appendix Table 2), though sediment Fe-P was not correlated with Fe across the lakes in general. The average proportion of Org-P and Ca-P in sediment TP were 23 % and 22 %, respectively, and neither of these fractions correlated with Fe-P. As expected, Org-P concentrations correlated strongly with LOI% ($r = 0.774$, $p < 0.001$). The highest contribution of Org-P to TP was observed in eutrophic Savijärvi (45 %) and in mesotrophic Lake Punelia (42 %), where Org-P is likely associated with the humic substances (water color values in the lakes were high, 70 and 45 mg/l Pt, respectively). The concentration of Fe-P correlated significantly positively with those of Mn and S (Appendix Table 2). Sediment Org-P concentration correlated significantly positively with the concentrations of Ca, Mn, and S, and negatively with

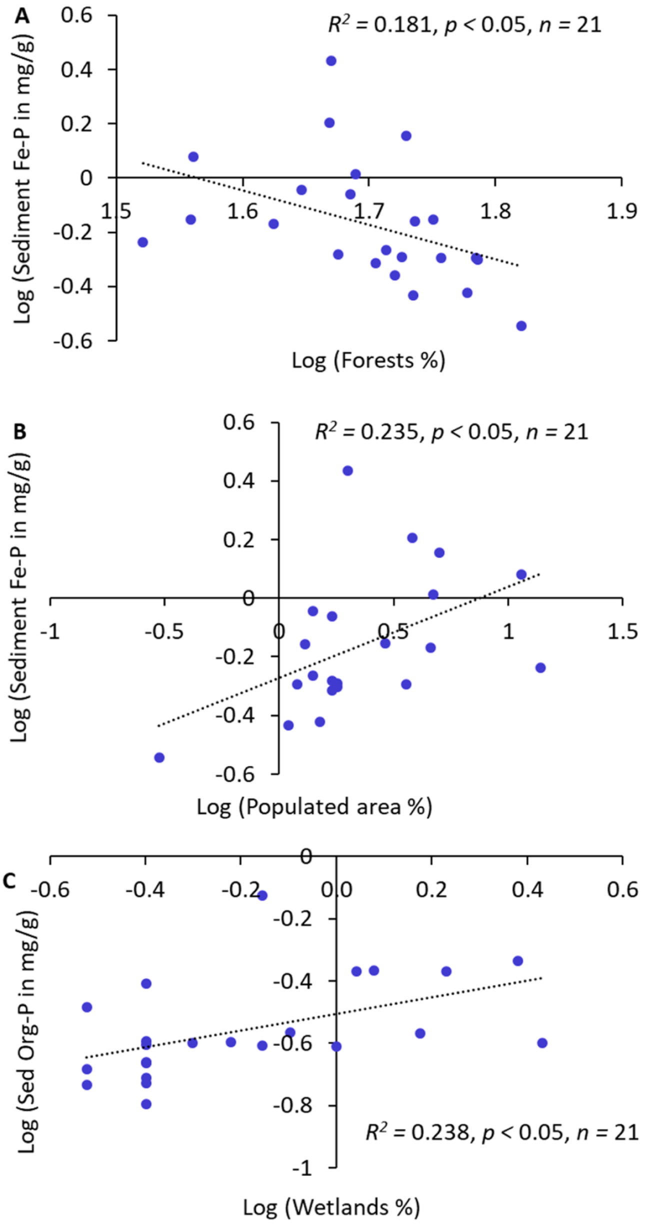

Fig. 2. Sediment (0–10 cm) Fe-P as a function of the forest area% (A) and populated area% (B) in the catchment. Sediment (0–10 cm) Org-P as a function of the wetland area% in the catchment (C).

the concentrations of Al, Mg, Cr. Significant correlations were found between many of the metals (Appendix Table 3). Most of these correlations were positive, suggesting similar origin within the catchment, or associated similar diagenesis in the sediment, e.g., with the sulfide cycle. Negative correlations were observed only for Mn and S, perhaps indicating their high reactivity.

Fe-P correlated significantly positively with the lake maximum depth and water residence time (Table 2), populated area%, and negatively with the forest% in the catchment (Fig. 2). All lakes with less than 10 % of field area (FA%) in their catchment basins (Hormajärvi, Punelia, Vitträsk, Katumajärvi and Oksjärvi) were mesotrophic and showed highly variable sediment Fe-P concentration and percent of TP (empty dots in Fig. 3). However, statistically significant relationships were observed for the lakes having FA% more than 10 (filled dots in Fig. 3; if Fe-P averaged over 10 cm sediments $R^2 = 0.178$, $p = 0.05$, $n = 22$; if Fe-P averaged over 20 cm sediments $R^2 = 0.299$, $p < 0.01$, $n = 22$). In these lakes, also Fe-P as TP% was statistically significantly related to the FA%, suggesting an impact of human activities. For all lakes, significant positive correlation was found between wetlands% and sediment Org-P (Fig. 2C).

External P loading (both in mg/m^2/y and in kg/y) was significantly related to FA% and FA/LA, as is expected from the results reported for the lakes of southern Finland by Horppila et al. (2019). Moreover, external P loading (in mg/m^2/y) correlated positively with the populated and paved areas relative to lake area (POP/LA and PAV/LA, respectively), and forest and wetland areas relative to lake area (FOR/LA and WET/LA, respectively). The corresponding relationships hold generally also for external P loading in kg/y, with the exception of FOR/LA and POP/LA. While the land use variables relative to lake area were related better to external P load (also if not expressed per lake area, excluding inflated correlation), the land use variables as percentage of the catchment area were related with the sediment P fractions (Table 2), indicating perhaps a role of the in-lake processes on the sediment P.

3.2. *Vertical changes in sediment components across 0–20 cm cores*

The Fe-P and TP concentrations decreased with the sediment depth in 12 lakes, and increased in one lake (Katumajärvi; Appendix Table 4). In ten of 12 lakes, where Fe-P decreased with depth, similar trends were observed also for Org-P. Significant positive correlation was found between Fe-P and Org-P ($r = 0.300$, $p < 0.001$, $n = 270$). Overall, 17 lakes (including Katumajärvi) showed a vertical decrease of the sediment Org-P concentration. Over all lakes, B and Ca decreased ($p < 0.001$ and $p = 0.007$, respectively), while Mg and Cr increased ($p = 0.004$ and $p = 0.010$, respectively) with sediment depth. Significant decrease in sediment Mn was found in ten lakes, and increase in one lake. The trends in the vertical changes of the other sediment components showed less consistency among the lakes. For example, S and Fe concentrations showed both decreases (e.g. in Hormajärvi) and increases (e.g. both Vesijärvi basins) with sediment depth.

3.3. *Internal P loading and lake water quality*

Internal P loading (IL) ranged from 24 mg/m^2/y in Lake Punelia to 864 mg/m^2/y in Enonselkä basin of Lake Vesijärvi, being on average 121 mg/m^2/y in mesotrophic lakes and 389 mg/m^2/y in the lakes of higher trophic status (eutrophic, hypertrophic). IL was related significantly positively to sediment Fe-P, Org-P and TP in eutrophic lakes (Fig. 4A, C, E). In mesotrophic lakes, IL correlated significantly with Fe-P and TP (Fig. 4B, F), but the effect of Org-P as a third variable turned non-significant. However, lake area as an additional variable (negative effect, partial $p = 0.025$) improved predictability of IL by 12.9 % ($R^2 = 0.481$, $p = 0.002$, $n = 27$ vs $R^2 = 0.352$, $p = 0.006$, $n = 27$). Similarly, water TP-dif, reflecting lake water TP concentration associated with internal P loading, varied depending on lake trophic state ($R^2 = 0.348$, $p = 0.002$, $n = 26$). TP-dif was correlated significantly to sediment Fe-P and TP in the eutrophic lakes, when data for Rehtijärvi and Enonselkä were excluded (Fig. 5A, E). In mesotrophic lakes, no significant relationships were found between TP-dif and sediment P forms. Relationships with IL indicate possible underestimation of TP-dif when comparing Figs. 4 and 5 in one case (Hormajärvi). The relationship between IL and TP-dif that is completely independently arrived at with respect to IL was much improved when data for Rehtijärvi, Enonselkä, Hormajärvi were excluded ($R^2 = 0.357$, $p < 0.01$, $n = 23$ compared to $R^2 = 0.159$, $p < 0.05$, $n = 26$; Fig. 6).

Both IL and TP-dif were significantly positively correlated to all studied phytoplankton variables, including Chl *a* (Fig. 7A and B), biomass of phytoplankton (Fig. 7C and D), proportion of cyanobacteria (Fig. 7E, F) and phytoplankton-based trophic state index (Fig. 7G and H).

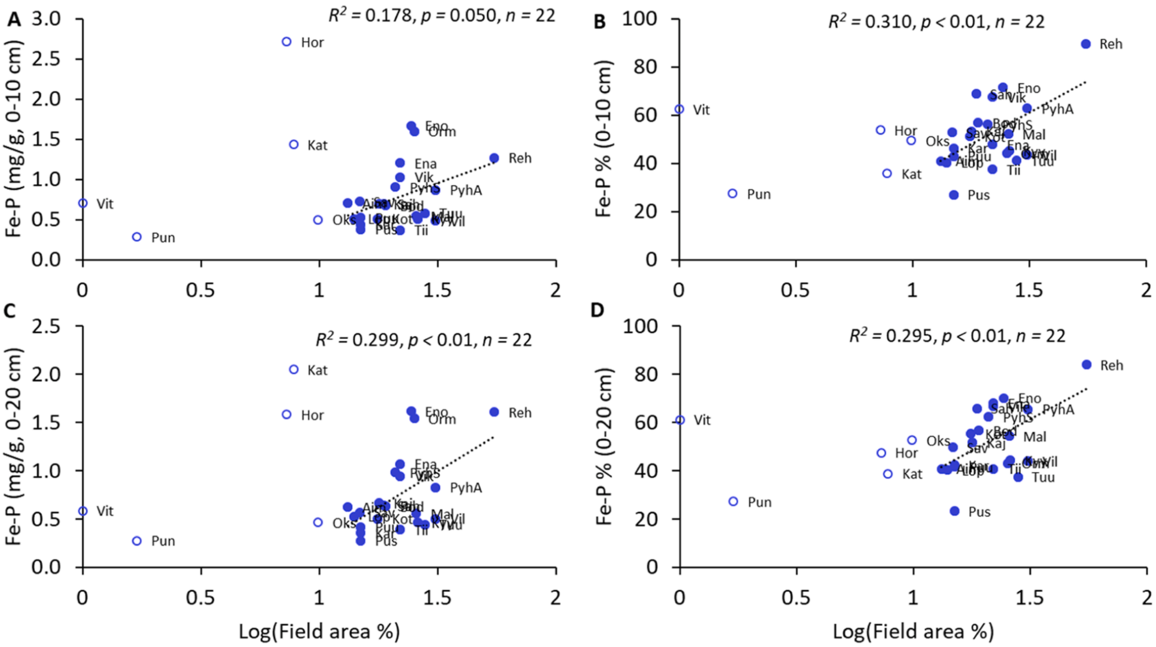

Fig. 3. Sediment Fe-P (left) and Fe-P% of total sediment P (right) as a function of the field area% in the catchment (FA%). The Fe-P and Fe–P% values are averages over 0–10 cm (A and B), and over 0–20 cm sediments (C and D). The lakes with the FA% less than 10 % are indicated with empty dots.

4. Discussion

4.1. Factors behind variations in sediment P characteristics

Lake sediment geochemistry is largely determined by catchment specifics (Tenhola, 1988; Albright et al., 2022; Lehtoranta et al., 2023; Waters et al., 2023). The high percentage of Fe-P in sediment TP, demonstrated in the current study, is often reported for Finnish lakes (Holmroos et al., 2009; Jilbert et al., 2020; Zhao et al., 2024). This phenomenon is most likely due to the lakes' location in southern Finland, where clay-rich soils from post-glacial subaqueous sediments contain high contents of Fe and Al oxides, which have a high P adsorption capacity (e.g., Łukawska-Matuszewska et al., 2013). Moreover, some of these soils have been exploited for agriculture and supplemented with additional P from fertilizers (Saarela, 2002). As shown here, the transport of Fe-P to the lakes is influenced by the percentage of the field area in the total catchment (Fig. 3). The influence of land use, especially agricultural, can be expected to be even larger closer to shore (as determined for the 100 m zone from shore; Szpakowska et al., 2022). Field areas are often associated with increased P losses from terrestrial soils (Röman et al., 2018), mainly due to erosion of soil aggregate-associated P and less due to leaching (Panagos et al. 2022). In our study, FA% was related not only to the sediment Fe-P concentration, but also to Fe-P%, supporting the interpretation of losses via erosion. Similarly, Räsänen et al. (2023) have identified high erosion agricultural lands near water bodies studied here, exporting 4030 to 10,820 kg soil/ha/y. Fe-P formation in catchments or lakes can also be accelerated by the high proportion and quantity of dissolved P in runoff from the fertilized areas (Hart et al., 2004; Ekholm et al., 2005). While streambed sediments may be considered as an important buffer between the land and onward delivery, these can also increase P transport (Simpson et al., 2021) through physical (during storms; Li et al., 2023) and chemical P release (Dupas et al., 2018). Likewise, higher external P load formed a larger pool of Fe-P in a mesocosm study where the mobile sediments P pool increased after increased external nutrient loading (Saar et al., 2022). In our study, Fe-P was not related to external P load directly, but was significantly correlated with FA%, in eutrophic and hypereutrophic lakes (i.e., when most of mesotrophic lakes were excluded). As FA% explained part of the variations in external P load, Fe-P of the lake sediments could also be affected by external P loading.

External P load originates also from catchment regions besides fields (Table 2). In general, much lower losses were reported for the forested areas than for the cultivated areas in Finland (Vuorenmaa et al., 2002), which can explain, why sediment Fe-P was found to be negatively correlated with the percentage of the forest area in the catchment (Table 2). P losses from the forested areas of the same magnitude (without anthropogenic impact, 9 mg/m^2/y) were reported for the lakes on the Canadian Shield (Nürnberg and LaZerte, 2004). On the other hand, forest areas, especially ditches in the study area can also supply lakes with an considerable amount of humic substances and Fe (Estlander et al., 2021; Härkönen et al., 2023), which may further sequester Fe-P (Tammeorg et al., 2022; Chen et al., 2024). Therefore, the effect of FA% on sediment Fe-P is more evident than the effect of the total external P load that includes also losses from other land uses. Of those, paved areas and wetlands can be associated with higher P export to lakes and contribute to their eutrophication, similar to what was reported by Nürnberg and LaZerte (2004). Further, the significant correlations between populated area% and sediment Fe-P indicate that the human impact of urban development is considerable along with the agricultural impact. Also, Kolath et al. (2024) have reported a significant correlation between the concentration of sediment mobile P and the percentage of impermeable land including urban areas, settlements, and roads in the catchment of Danish lakes.

To our knowledge, this is the first time when a relationship between FA% and sediment P variables was established based on a large amount of data. Only scarce supporting evidence relating land use practices in the catchment with lake sediment composition can be found in the literature including data reported for seven shallow glacial lakes in northwest Iowa (USA; Albright et al., 2022) and a eutrophic catchment in central Sweden (Lannergård et al., 2020). In those sediments, however, Fe-P (redox-sensitive P) was not the dominating fraction, and thus, comparison of the reported results with our findings is limited. Nevertheless, Łukawska-Matuszewska et al. (2013) found that the dominant P pool in sediments near the inlets of agriculturally influenced streams in the catchment of a eutrophic lake in southeastern Norway was non-apatite inorganic P (including Fe-P). Our findings would also serve as a mechanistic explanation for the relationship between field area% and sediment P release demonstrated by Carter and Dzialowski (2012).

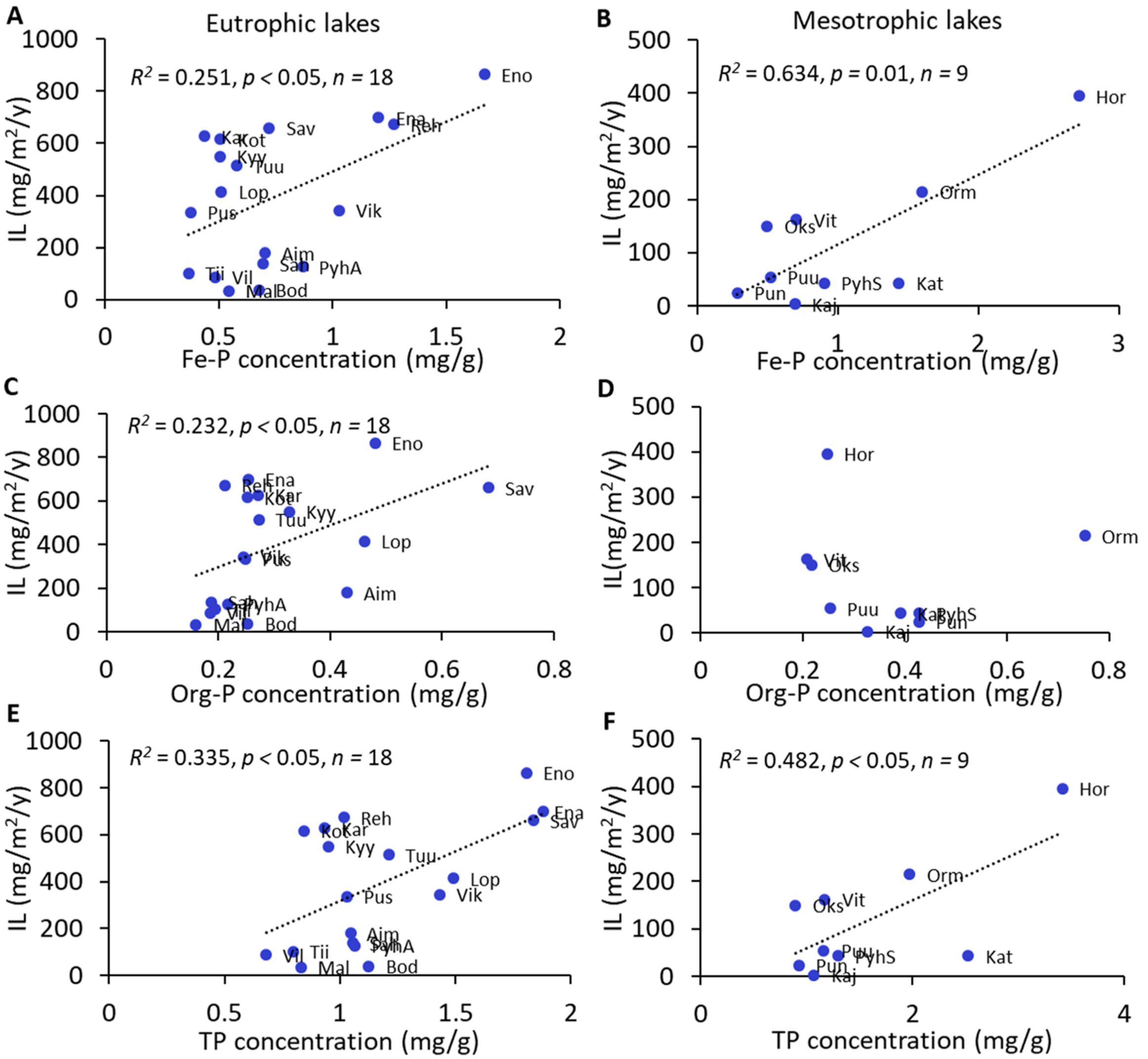

Fig. 4. Internal P load (IL) as a function of sediment Fe-P, Org-P, and TP concentration (0–10 cm average) in 15 eutrophic and three hypertrophic lakes (left: A, C, E) and in mesotrophic lakes (right: B, D, F). Trendlines are shown only for significant relationships. Letters indicate names of the lakes studied.

According to our results, lakes with larger maximum depth and longer water residence time had also a larger pool of sediment Fe-P. These findings agree with the trends reported in the literature that show that both, depth and residence time, support P accumulation in sediments (Albright et al., 2022; Tammeorg et al., 2022; Waters et al., 2023). In addition, these factors may determine the processing of P within the sediment, and most P retention models in mass balance models depend on annual water load or residence time (e.g. Nürnberg, 1988). An increase in Fe-P concentration towards the sediments surface indicates a role of diagenetic transformations that almost continuously regenerate P that can be released into the water column at favorable conditions (i.e., increased temperature and decreased redox potential). Diagenetic transformations also affect Org-P (and other associated chemical variables, e.g. Mn, S) that were significantly positively related to Fe-P. Specifically, Fe-P (as a proxy of P adsorbed to Fe hydroxides) and Mn (as a proxy for Mn oxides) are expected to be correlated across the whole dataset, because both components are susceptible to redox-related geochemical focusing (e.g. Schaller et al., 1997) and can be co-enriched in specific bathymetric settings. When these settings are deep areas of lakes where fine-grained autochthonous organic material accumulates and sediments are organically enriched (eutrophic) with very low redox potential, rates of sulfate reduction are high and lead to the formation of sulfide minerals in the sediments. These mechanisms can explain the correlation between Fe-P, Mn and S in these lake sediments.

In addition to diagenetic transformation, increased pools of mobile P close to the sediment surface have been attributed to increased eutrophication (e.g., Carey and Rydin, 2011). Most of the study lakes showing an increase in sediment P towards the surface do not have long-term series of external P loading of high resolution. Nevertheless, decreases or no changes in external P loading are reported for most lakes (e.g. Ekholm et al., 2015). For example, the external P load to Tuusulanjärvi, a lake with relatively high proportion of human-impacted areas (proportion of urban, paved and field areas) was reported to decrease (Horppila et al., 2017) while the concentrations of Fe-P, Org-P and TP showed an increase towards the sediment surface (Table 2). Evidence for the upward diffusive P flux towards the surface sediments (remineralization of organic matter and associated dissolution of Fe–Mn oxides) was provided also for the Enonselkä basin of Lake Vesijärvi recovering from eutrophication caused by urban developments (Jilbert et al., 2020). The enrichment of the basin in the past also agrees with the higher S precipitation in the past (higher S and Fe concentrations deeper in sediments). In lakes that displayed a decrease in P towards the sediment surface, the higher concentrations of metals, such as Cd, Cr, Zn, Co, Ni in deeper sediment layers suggest higher human impact in the past. Hence, higher legacy P is found in lakes with higher water residence

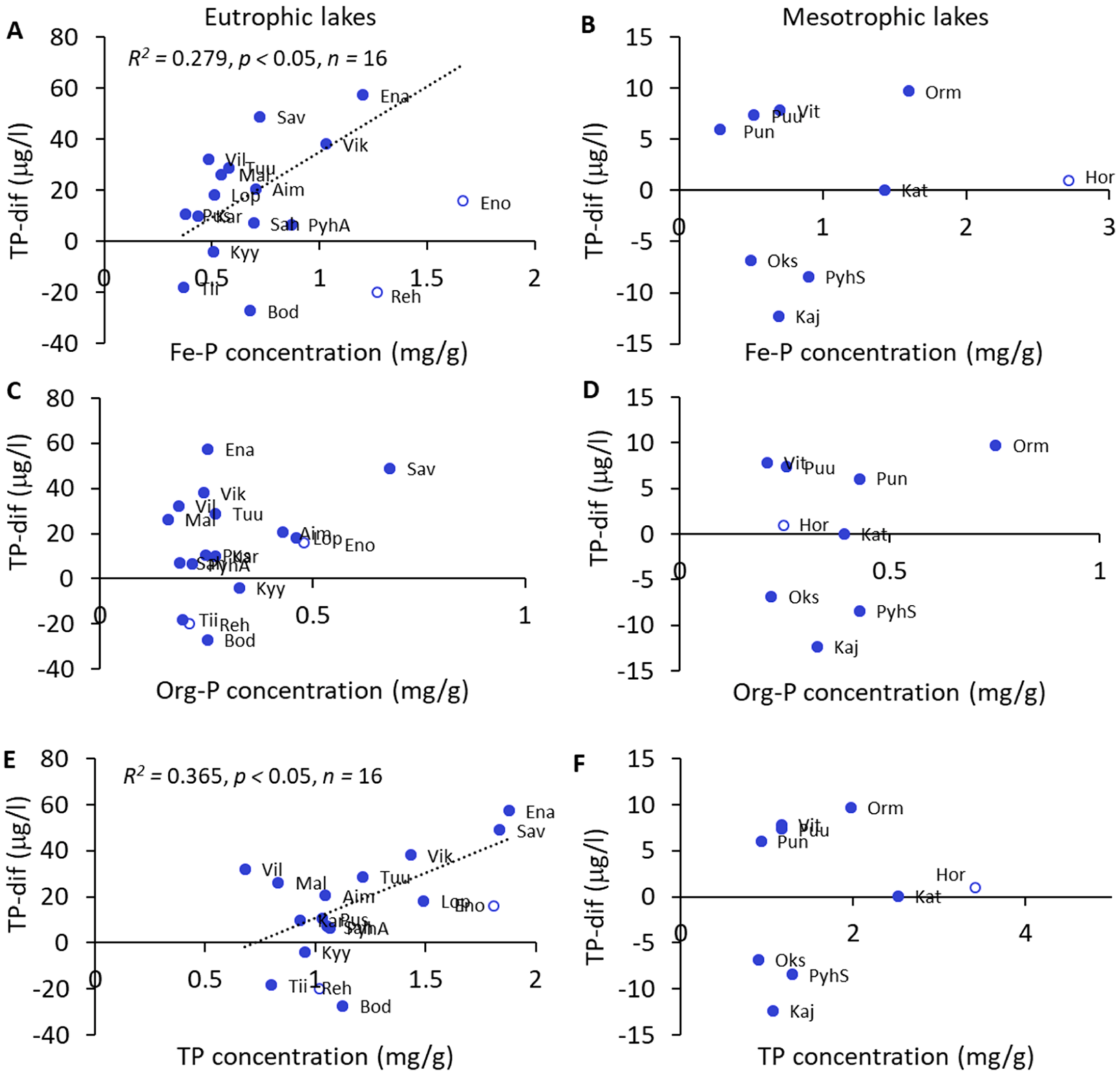

Fig. 5. Lake water TP concentration ascribed to internal P load, i.e. TP-dif (determined from the difference between observed and predicted TP concentrations in lake water) as a function of sediment Fe-P, Org-P, and TP concentration (0–10 cm average) in eutrophic (left: A, C, E; three hypertrophic lakes are also included in this set) and mesotrophic lakes (right: B, D, F). Empty dots indicate lakes that disagree with the data in Fig. 2 (outliers, including Rehtijärvi, Enonselkä and Hormajärvi). Trendlines are shown only for significant relationships, when outliers are excluded.

time and lake depth that can be recycled to the water column for decades (Sharpley et al., 2013).

4.2. *Effects of sediment P on internal P loading and water quality*

We demonstrated the importance of the sediment P pool to internal P loading: sediment Fe-P, Org-P and TP were shown as a potential source for internal P load (Fig. 4). Org-P was no longer retained in the linear model for predicting IL if TP in lake water as a trophic state variable was included as the first variable and sediment Fe-P as the second variable. Sediment Fe-P and TP that was mostly comprised of Fe-P (55 % on average) were strongly correlated with internal P loading in both eutrophic and mesotrophic lakes. While the role of Org-P was apparent in sediment P release in eutrophic lakes, such evidence was missing for the mesotrophic lakes. This finding suggests implications of humic substances, because seven of nine mesotrophic lakes studied here were humic. A significant correlation between Org-P and wetland% indicated that the organic matter could be partially of allochthonous origin. Several studies have shown that humic substances have a negative effect on the sediment P release rate (Nürnberg, 1988; Tammeorg et al., 2022; Chen et al., 2024). However, the lack in predicting IL by Org-P can also be explained by a mere supportive role of Org-P in sediment P release, where the mineralization of organic matter decreases the redox potential at the sediment surface contributing to the reductive dissolution of Fe-P compounds. Org-P was still of much smaller portion relative to Fe-P in the sediments of the lakes studied here. Moreover, the mere supporting role of Org-P in sediment P release was also demonstrated in several other eutrophic lakes of southern Finland (Zhao et al., 2024).

Generally, similar trends held also for TP-dif (reflects lake TP concentration from internal P load), supporting the role of redox-related P release in internal P loading (Figs. 5 and 6). The relationships between sediment Fe-P (and TP) and TP-dif are significant for the set of eutrophic lakes when data for Rehtijärvi and Enonselkä were excluded. In the set of mesotrophic lakes, relatively low TP-dif values disagreed with the high sediment TP values in Hormajärvi. Relative to the other stratifying lakes studied here (including also Hormajärvi and Enonselkä), Rehtijärvi has exceptionally high water-column stability due to its morphology. Morphometric ratio (14.8 m/km) is much higher than in the rest of the lakes (varied from 0.4 to 5.8 m/km), which delays the mixing of sediment released-P into the surface water layer, and renders

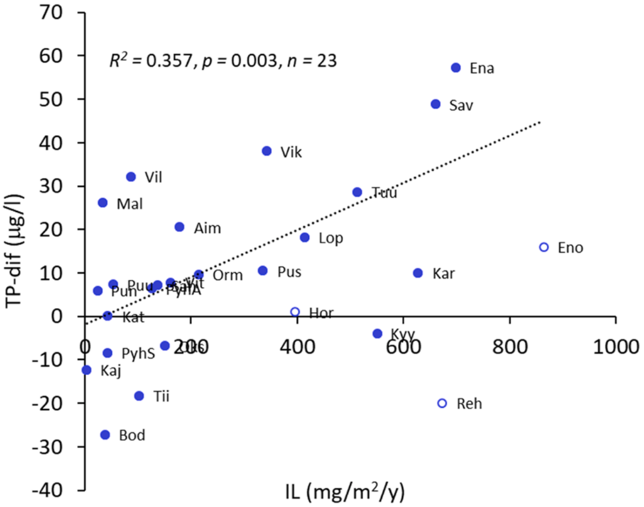

Fig. 6. Relationship between internal P load and lake water TP concentration ascribed to internal P load, TP-dif (determined from the difference between observed and predicted TP concentrations in lake water) for all lakes. Empty dots indicate outliers (including Rehtijärvi, Enonselkä and Hormajärvi), and trend is shown for the relationship without those outliers.

the observed TP concentration relatively close to the predicted TP value. It is no surprise that IL calculated by multiplying AF values and release rate would result in higher estimates than can be expected from the TP-dif. Comparatively low TP-dif in relation to sediment Fe-P in Enonselkä and Hormajärvi can be explained by the impact of hypolimnetic aeration that would help accumulate Fe-P. In Enonselkä, more apparent effects of aeration on hypolimnetic oxygen and P concentrations were reported for cool winters and summers (Horppila et al., 2015). Hypolimnetic phosphorus concentration was stabilized to a lower level than before the aeration (Salonen et al., 2023). Clear benefits (decreases) of aeration for hypolimnetic oxygen and phosphorus were reported for Hormajärvi (Vesterinen, 2021). Thus, aeration could lower observed TP values and thus the difference between TP observed and TP predicted is low, while the IL method is not sensitive to this fact, because it is based on in situ observations. In general, different restoration activities have taken place in almost all of the study lakes (Tammeorg et al., 2018). However, these measures likely had only a short-term effect (or no effect), or were carried out for too short periods (we used long-term averages in our study) to influence the calculation of TP-dif, like in Hormajärvi or Enonselkä. For example, in Tuusulanjärvi biomanipulation was shown to be effective, but further reduction of external P loading was still the first priority (Horppila et al., 2017).

Internal P load has a high impact on lake water quality (Fig. 7), and thus measures addressing internal P load are needed to promote water quality improvement. Internal P loading comprises a considerable portion of the whole P loading in many lakes, and high implications for lake water quality are expected (Nürnberg, 2009). The internal P load supplies phytoplankton with the nutrient in a readily available form (phosphate), and often at times when external nutrient loads are low (Nürnberg et al., 2013; Bormans et al., 2016). An increasing number of studies relates internal P loads or associated sediment variables with phytoplankton biomass (Nürnberg et al., 2013; Rahman et al., 2022), chlorophyll *a* (Chl *a*) concentration (e.g., Horppila et al., 2017; Tammeorg et al., 2017; Albright et al., 2022; Waters et al., 2023), frequency of algal blooms (Waters et al., 2021), and cyanobacteria biomass (e.g., Tammeorg et al., 2023; Swann et al., 2024). Cyanobacteria take easily advantage of internal P load at warm water temperatures and conditions, and thus are particularly favored by the sediment P release (Istvánovics et al., 2002; Nürnberg et al., 2013; Bormans et al., 2016). The impact of the sediment-released P is much determined by the mixing conditions, and thus may not be as obvious in deeper stratifying lakes as in shallow lakes (Søndergaard et al., 2017). Nevertheless, P is exchanged between hypolimnion and epilimnion by diffusion and convection and entrainment during the stratification period. Moreover, stratification disturbances due to storm events are often observed (Niemistö et al., 2012). In general, the lakes studied here are still relatively shallow (average mean depth for the study lakes is 5 m), and the generally low morphometric ratio (average for the study lakes is 3 m/km) suggests relatively weak water column stability. Similar conclusions were also reached for several other stratifying lakes, explaining the limited success (no Chl *a* decline) of hypolimnetic aeration in lake water quality management (Tammeorg et al., 2017; 2020). Water column stability may be stronger in smaller lakes possibly explaining, why the prediction of internal P load in regression model having trophic state as a first variable and sediment Fe-P as the second variable was improved by the lake area size (third variables with a negative effect). Water column stability may be further supported by higher water color in smaller lakes (Kortelainen, 1993; Kortelainen et al., 2004).

Previous analyses of internal P loading data for numerous lakes in southern Finland (including 23 lakes of the current study) using empirical models suggested the large role of redox-related P release in the P budget (Tammeorg et al., 2020). In the current study, we provided a link between water quality and internal P load based on comprehensive sediment data for a range of trophic and morphometric conditions. Being the dominant sediment P form in most of these lakes, Fe-P was the main contributor to the mobile P pool. Similarly, in the model developed by Waters et al. (2023) based on spatially comprehensive sediment and water quality data, redox-sensitive P was the most critical geochemical variable that had a strong effect on the trophic state index. Together these findings support a number of models developed by Nürnberg (2020) that assume a large role of redox-related P release in internal P loading, supporting their general applicability and thus their importance in lake water quality management. The results of the current study identified additionally the linkage with the % of the field area in the catchment, which allows us to suggest that reducing P losses from the fields would lead to the reduction of internal P loading in lakes and thus would improve lake water quality. Moreover, decreasing P losses from the urban areas will likely reduce the formation of releasable P (as Fe-P) and subsequent sediment P release. Hence, internal P loading and its implications for lake water quality may be well-predicted from the catchment developments, similar to what was proposed earlier by Nürnberg and LaZerte (2004).

5. Conclusions

Our analysis of 27 lakes in southern Finland revealed a link between land use in the catchment, internal P load and lake water quality through sediment Fe-P. In eutrophic lakes with more than 10 % of the catchment area covered by fields (FA%), sediment Fe-P increased with increasing FA%. Similar trends were also found for Fe-P%, suggesting the governing role of erosion in P losses from agricultural areas. Moreover, populated areas in the catchments contributed to the pool of Fe-P. Fe-P was found the main sediment variable explaining the variation of internal P load in both eutrophic and mesotrophic lakes. These trends were supported by the relationships between Fe-P and TP-dif, i.e., the lake water TP concentration determined as the difference between observed and predicted water TP values and ascribed to sediment P release. The high impact of internal P load was demonstrated by significant relationships between IL and several lake water quality variables, including phytoplankton biomass, percentage of cyanobacteria, Chl *a* concentration and trophic state index. Field and populated areas in the catchment were found to increase the pool of releasable P (influencing P release rates). Hence, land use enables to predict not only external P loading, but also internal P loading and its implications for lake water quality. This study provides mechanistic evidence for the legacy accumulation of external P in lake sediments.

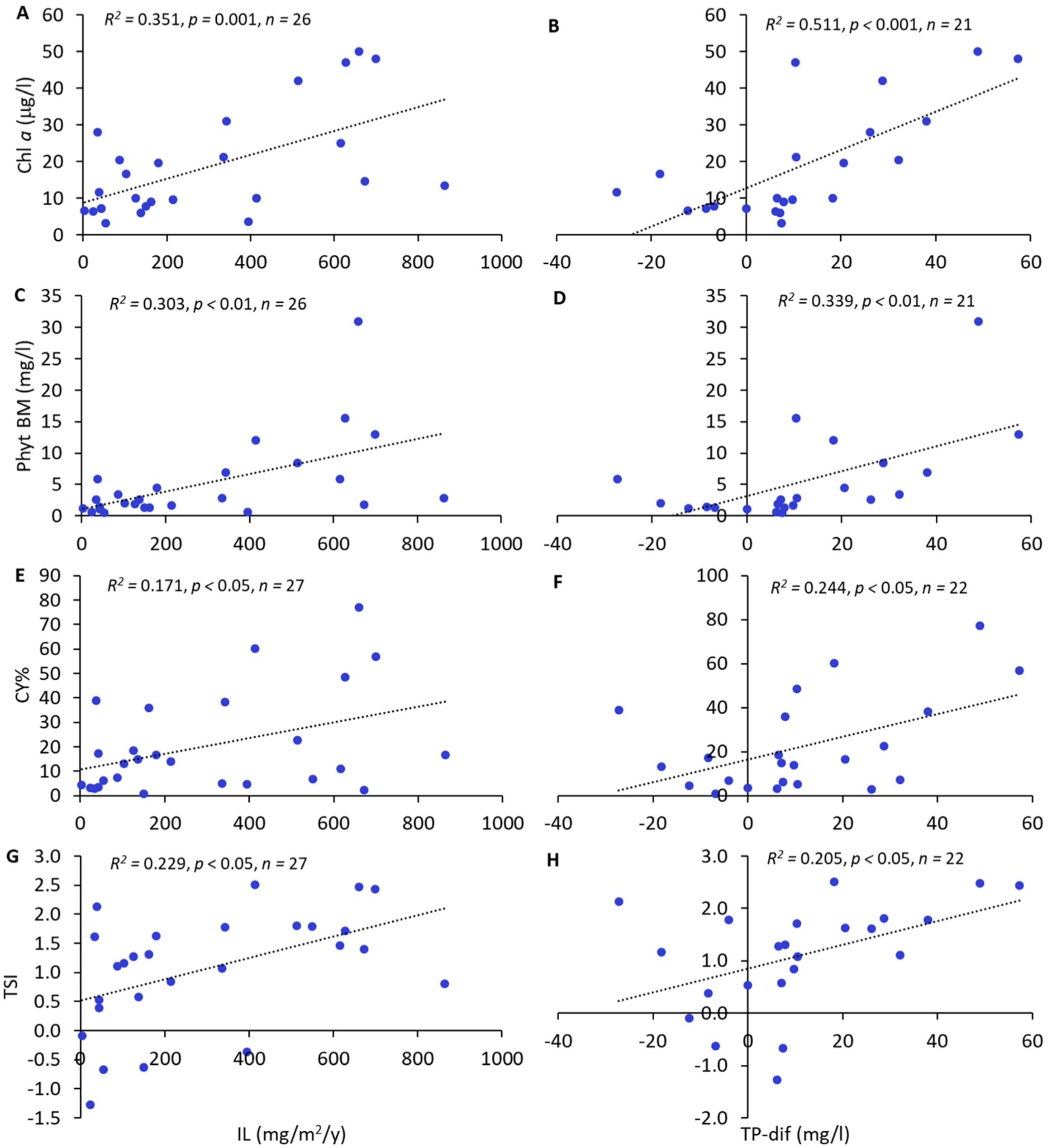

Fig. 7. Chlorophyll *a* concentration, phytoplankton biomass, proportion of cyanobacteria (CY%) and trophic state index (TSI) as a function of 1) internal P load (IL; left A, C, E, G); 2) lake water TP concentration ascribed to internal P load (TP-dif, determined as the difference between the observed and predicted TP concentrations in lake water) (right B, D, F, H).

CRediT authorship contribution statement

Olga Tammeorg: Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Gertrud K Nürnberg:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Jukka Horppila:** Writing – review & editing, Validation, Investigation. **Priit Tammeorg:** Writing – review & editing, Validation, Investigation. **Tom Jilbert:** Writing – review & editing, Resources. **Peeter Nõges:** Writing – review & editing, Validation, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.122157.

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